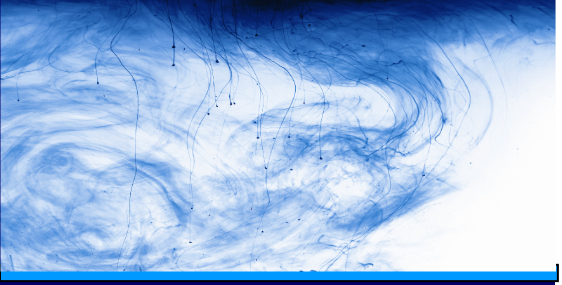


CHEMSYSTEMS
PERP PROGRAM

Report Abstract

Alpha Olefins
PERP06/07-5

April 2008

Nexant

CHEMSYSTEMS PERP PROGRAM

Report Abstract

Alpha Olefins
PERP06/07-5

April 2008

Nexant

www.chemsystems.com

The ChemSystems Process Evaluation/Research Planning (PERP) program is recognized globally as the industry standard source for information relevant to the chemical process and refining industries. PERP reports are available as a subscription program or on a report by report basis.

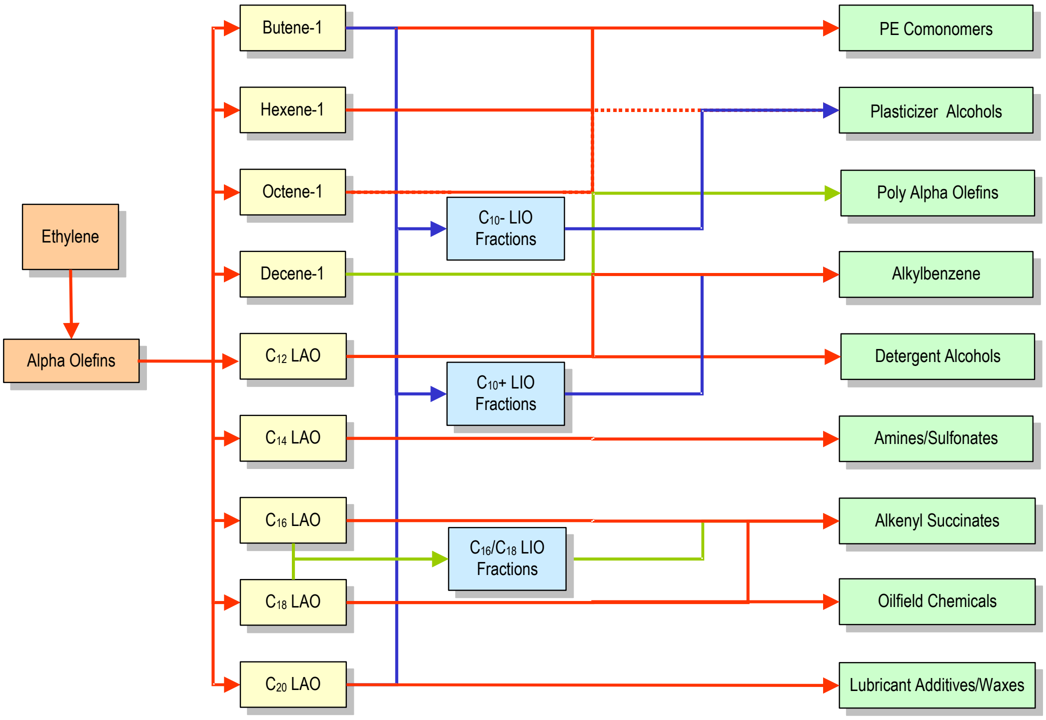
For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.chemsystems.com.

1 INTRODUCTION

The alpha olefins business is complex. A full range alpha olefins plant produces, depending on technology, a range of olefins with even numbered carbons. As Figure 1 illustrates, alpha olefin producers serve the markets of polyolefins, synthetic lubricants, detergent intermediates, oilfield chemicals, paper industry, additives, etc. Each derivative market has its own characteristics in terms of demand growth, selling geography, customer base, customer fragmentation, quality requirements, off-take volumes, etc. Even a naphtha cracker with its multiplicity of products, ethylene, propylene, C_4s, aromatics, etc, does not serve markets with such different characteristics.

Figure 1 Schematic View of the Alpha Olefins Business

(Illustrative)



Q108_00101.0007.4105.vsd/F2.1

The business of managing an alpha olefins business is therefore a challenge of balancing the requirements of serving the markets while maximizing revenue across the whole spectrum of alpha olefin products.

2 TECHNOLOGY

Overall, the technology for alpha olefins production (greater than C_2 and C_3) is divided into two families:

- Full-Range Alpha Olefins (both commercial and new/emerging processes)
- Single-Fraction or On-purpose Production (both commercial and new/emerging processes)

2.1 Full-Range Technologies

Full-range technologies cover those processes based on ethylene oligomerization that produce alpha olefins from butene-1 through to C_{30}+. Different technologies in commercial operation today vary in their design and provide a maximum limit on carbon number.

The commercial technologies discussed in this report are:

- Chevron Phillips GULFTENE® process
- Shell SHOP process
- INEOS process (originally developed by Ethyl)
- Idemitsu process

There are three core technologies for the production of alpha olefins which are owned and operated at world-scale, namely those of INEOS (formerly BP, formerly Amoco, formerly Albemarle and formerly Ethyl), Chevron Phillips (formerly Chevron and formerly Gulf) and Shell. Smaller units using different albeit similar technologies are operated by Mitsubishi and Idemitsu in Japan only. Both INEOS (as Albemarle) and Chevron Phillips (as Chevron) have licensed their processes to Nizhnekamsk (Siberia) and Spolana (Czech Republic) respectively. In 2003, the Spolana facility closed.

Not only does each process operate with a different approach to catalysis and therefore distribution, but the reaction systems are quite different. However, once an alpha olefin stream is produced with catalyst removed, the separation train is generally similar in concept. The clear exception is Shell which includes metathesis in its process technology.

In recent years, the drive to develop more advanced polyethylenes using metallocene catalysts has made extra demands on comonomer alpha olefin quality. To fulfill these demands, additional distillation steps have been included in alpha olefin plants for upgrading the quality of hexene-1 and in some cases the quality of butene-1 by removing trace benzene, for example. These enhancements are referred to as “Super Six” and “Super Four” columns, respectively.

2.1.1 Chevron Phillips Process

In the Chevron Phillips full-range process (originally developed by Gulf, which subsequently merged with Chevron), alpha olefins are synthesized from ethylene using Ziegler chemistry. Since Chevron buys its triethylaluminum, there are two basic steps to the olefin synthesis process: chain growth and displacement.

The Chevron Phillips process, operated at Cedar Bayou, TX and licensed to Chemopetrol, Spolana Neratovice, uses the single-stage combined growth and displacement technique. During displacement, the alkyl groups are cleaved as straight-chain alpha olefins with an even number of carbon atoms. They are obtained in high purity because little isomerization takes place under the reaction conditions.

In the Chevron Phillips process, only a catalytic amount of alkylaluminum is employed. Several chain-growth displacement sequences occur on each aluminum bond during each pass through the reactor. The alkylaluminum can be destroyed after the reaction without undue economic penalty. Alkali hydrolysis converts the catalyst to an aluminate, which facilitates separation and avoids production of by-products during olefin recovery.

A characteristic of the single step process is its broad carbon number distribution. A typical weight distribution will follow a reduced geometric series, increasing in molecular weight from C_4. Raising the reaction pressure will extend the series and produce a larger $C_{12}+$ segment. A theoretical weight distribution can be derived, assuming the only reactions are chain growth and chain displacement by ethylene. The theoretical product chain length distribution is governed by the single parameter, K, which is the ratio of chain growth reaction to displacement reaction under the particular reaction conditions.

2.1.2 Shell Higher Olefins Process (SHOP)

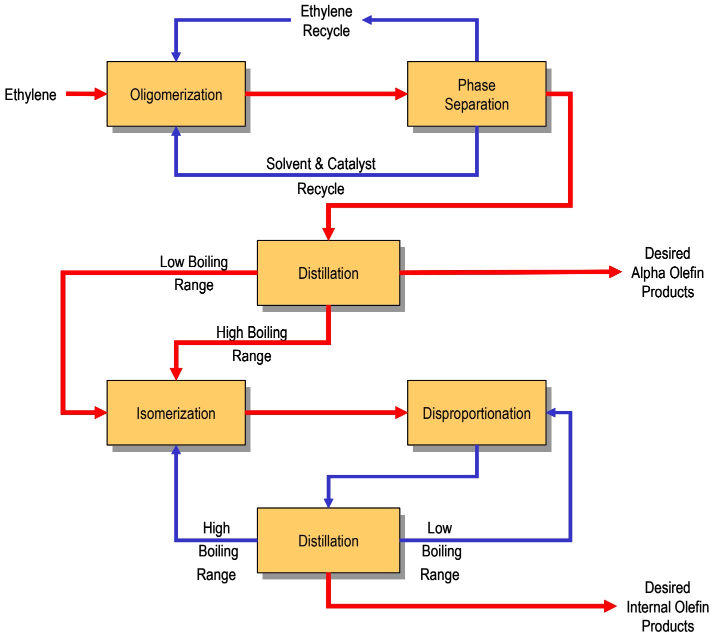
The Shell Higher Olefins Process (SHOP) employs a series of different process chemistries to circumvent the problems associated with the normal geometric distribution of ethylene oligomers:

- Oligomerization
- Isomerization
- Olefin Disproportionation (Metathesis)

This sequence of processing steps allows production of the most economical chain lengths to be maximized to suit Shell's strategy of combining alpha olefins with synthetic detergent alcohols production. A simplified block flow diagram of the SHOP process is shown in Figure 2.

Figure 2 Overview of Shell's Higher Olefin Process

(Illustrative)



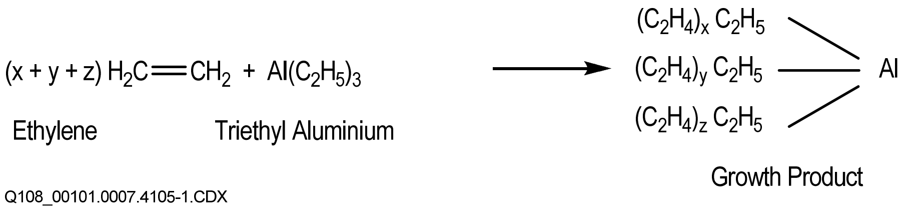
Olefin disproportionation or olefin metathesis is a key and distinguishing feature of the SHOP process. This unusual chemistry typically takes place over heterogeneous catalysts comprising molybdenum, tungsten, or rhenium on alumina or silica substrates. Homogeneous catalysts are known, but are not usually commercially employed. The metathesis step allows the low and high boiling range internal olefins to be disproportionated into a range of more useful molecular weight olefins. For example, a C_4 olefin and a C_{24} olefin can be disproportionated into two C_{14} olefins. [A more recent example of olefin metathesis is the commercialization of olefin metathesis for propylene production from ethylene and butene-2.]

2.1.3 INEOS Process

The INEOS process employs both a catalytic step and a stoichiometric stage. The technology was originally commercialized by Ethyl and through subsequent mergers and acquisitions came under BP ownership via Albemarle and Amoco. At the end of 2005, INEOS acquired the Innovene assets from BP. By recycling alpha olefins to the chain growth section, INEOS can peak production of olefins in the carbon range desired, though this introduces a degree of branching into the alpha olefin product. Three basic steps are used to synthesize alpha olefins from ethylene by means of Ziegler chemistry:

- Triethylaluminum (TEA) synthesis
- Chain growth
- Displacement

TEA, which is the catalyst for ethylene chain growth, is prepared by reductive alkylation of aluminum powder with hydrogen and ethylene. Ethylene chain growth occurs catalytically via stepwise addition to each of the three alkyl groups of the TEA:



$$(x+y+z)\,H_2C{=}CH_2 + Al(C_2H_5)_3 \longrightarrow Al\left[(C_2H_4)_x C_2H_5\right]\left[(C_2H_4)_y C_2H_5\right]\left[(C_2H_4)_z C_2H_5\right] \qquad (9)$$

By means of controlling the rate of ethylene addition and temperature, chain growth can be somewhat regulated. Yielding a broad carbon number range product, this one step process is the first stage in the INEOS process. INEOS typically runs this process in order to yield a large proportion of low molecular weight C_4-C_8 olefins. This product range is needed for use in INEOS' complementary second step and to meet comonomer market demand.

Unlike many areas of the petrochemical industry, LAO technology was historically not available via license. However, this is changing and several licensors are now offering LAO technology. These new full- range technologies are discussed in this report:

- Axens ALPHASELECT®
- UOP LINEAR-1®
- SABIC/Linde α-SABLIN®

2.2 Single Fraction or On-Purpose Technologies

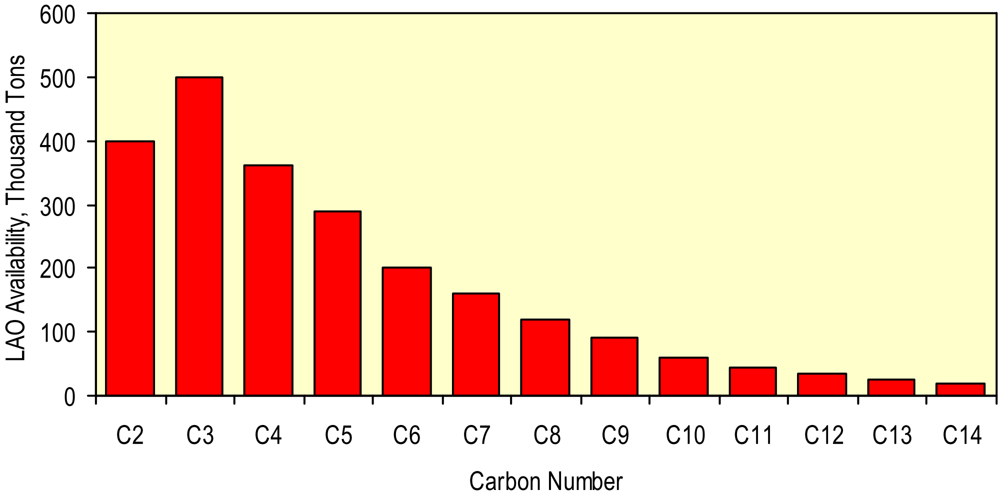
2.2.1 *Sasol Fischer-Tropsch Derived Hexene-1 and Octene-1*

Sasol, the largest chemical producer in South Africa, began recovering pentene-1 and hexene-1 from its coal-to-synthetic fuels complex at Secunda in the early 1990s. While only minor quantities of pentene-1 have actually been produced, Sasol has become a major global supplier of hexene-1 and now also octene-1. Sasol commenced hexene-1 production in 1994 and has since expanded capacity. Sasol expanded its alpha olefin portfolio and brought on-stream its first octene-1 line in 1998 with a capacity of 48 thousand metric tons per year. Sasol success in penetrating the ocente-1 market, has spurred Sasol to build a second octene-1 train in 2004 of 48 thousand metric tons per year.

The Secunda complex processes coal-derived synthesis gas in its Synthol reactors to yield hydrocarbon streams rich in alpha-olefins - in addition to gasoline, diesel, and other fuel products; oxygenates; and lower molecular weight olefins such as ethylene and propylene. The Synthol product streams contain a range of alpha-olefins of all carbon numbers (odd and even) from ethylene through decene-1. Availability generally decreases with increasing carbon number. Quantities potentially recoverable in the butene-1 to octene-1 range used as polyethylene comonomers, as depicted in Figure 3, are significant relative to quantities produced by ethylene oligomerization units.

Figure 3 Sasol FT-Derived Alpha Olefin Distribution

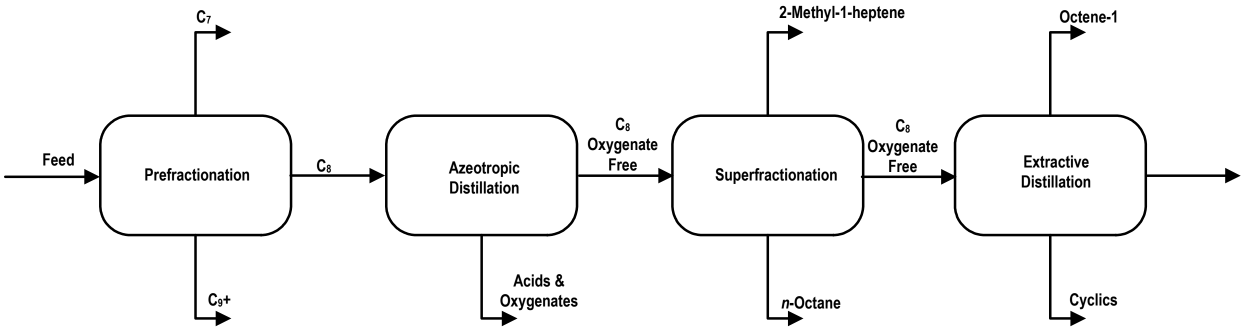
(Weight percent)



Q108_00101.0007.4105-Charts.xls\F4.6

Unfortunately, owing to the complex mixture of isomers and oxygenated compounds, it is not possible to isolate hexene-1 or octene-1 by simple distillation. This prompted Sasol to develop separation schemes involving a number of steps including etherifications, extractive distillations, and superfractionations. For example, Sasol's most recent separation scheme is its octene-1 Train II as outlined in Figure 4.

Figure 4 Sasal Fischer-Tropsch Process



Source: Sasol

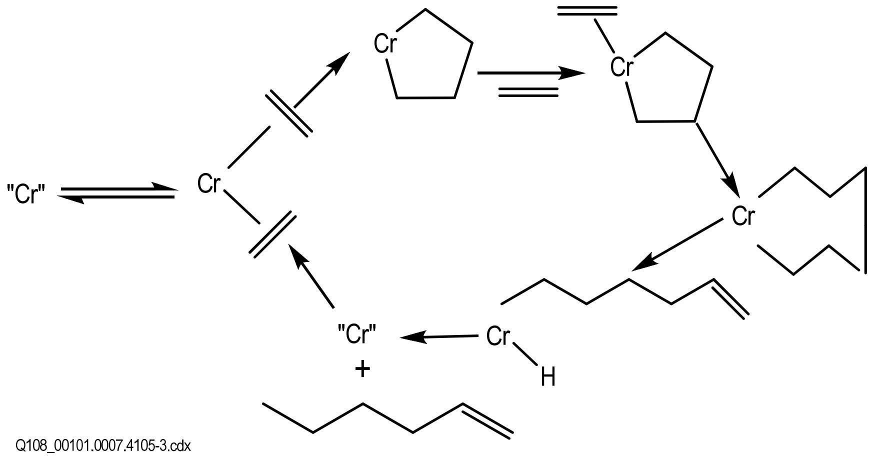
Q108_00101.0007.4105-Figures-1.vsd/F4.15

2.2.2 *Chevron Phillips Ethylene Trimerization to Hexene-1*

Phillips, prior to its merger with Chevron (to form Chevron Phillips), developed a family of chromium-based catalysts which can selectively trimerize ethylene to hexene-1 with high selectivity. In order to achieve such high selectivity, a fundamentally different chemical pathway must be at work compared to full range technologies.

The key difference between this catalyst system and conventional oligomerization catalyst is the propensity of the Phillips chromium based catalyst to form metallacycles (See Figure 5). The first metallacycle formed is a five-membered ring structure comprising two equivalents of ethylene. Five-membered rings are thermodynamically relatively stable structures and remain intact long enough for another equivalent of ethylene to be inserted thus affording a seven-membered metallacycle. At this stage in the catalytic cycle the seven-membered ring structure decomposes via reductive elimination, in preference to forming a relatively unstable nine-membered ring, and releases one equivalent of hexene-1 and an active catalyst poised to repeat the cycle. The overall reaction is thus:

Figure 5 Trimerization Catalysis
(Illustrative)



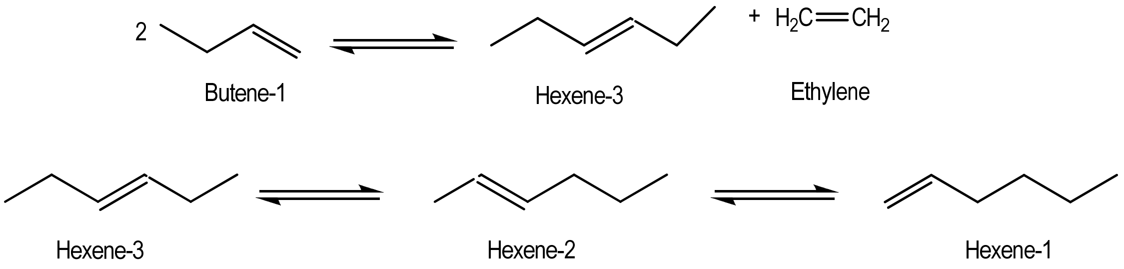
Q108_00101.0007.4105-3.cdx

In 2003, Chevron Phillips started up a 47,000 metric ton per year hexene-1 only plant in Qatar as part of its Q-Chem venture. Sinopec's Yanshan Petrochemical has recently developed its own proprietary ethylene trimerization process and has built a 50,000 metric ton per year hexene-1 plant. This plant was scheduled for start-up in the second half of 2007. And now, Mitsui Chemical has announced the development of its own ethylene trimerization process.

2.3 Emerging On-Purpose Processes

2.3.1 Lummus Comonomer Production Technology (CPT)

Lummus has been quite successful in developing and licensing its metathesis-based Olefins Conversion Technology (OCT) for on-purpose production of propylene. Lummus has also been developing alternative uses for metathesis technology. One of these developments is termed Comonomer Production Technology (CPT). CPT has several options, but the main aspect assessed in this report is for on-purpose production of hexene-1. This process employs the so-called auto-metathesis of butene-1 to give hexene-3. The hexene-3 is isomerized to finally give hexene-1. The idealized chemical reactions are shown.

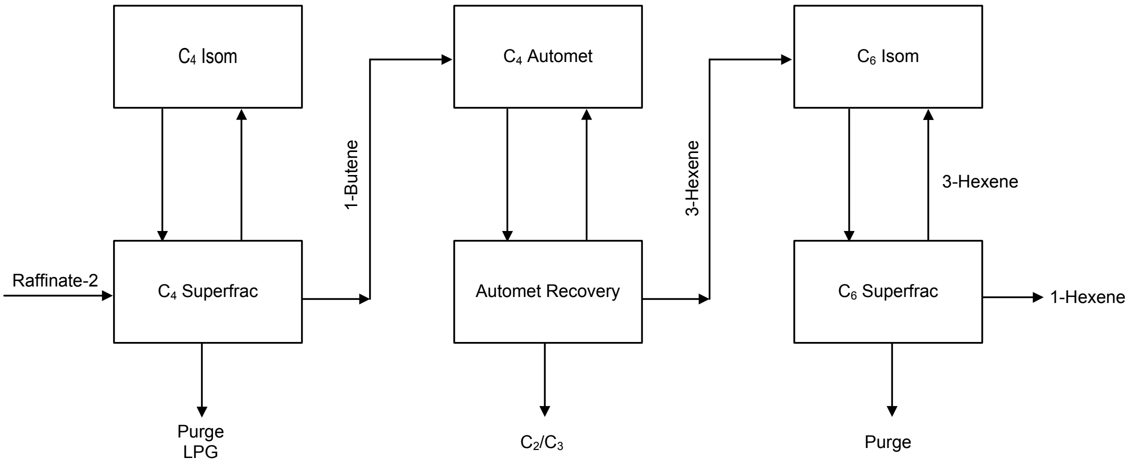


Q108_00101.0007.4105-4.CDX

A challenge to this approach is that both the metathesis and isomerization reactions are equilibrium controlled and can lead to side products and extensive recycle loops.

Figure 6 provides a simplified block flow diagram of the Lummus CPT process.

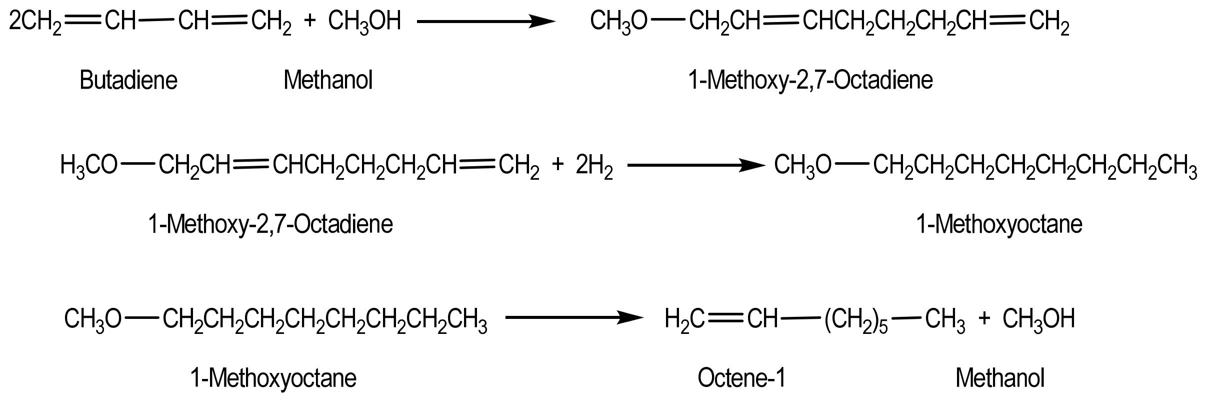
Figure 6 Simplified Block Diagram of Lummus CPT Process for Hexene-1 Production



Q108_00101.0007.4105_Figures-1.vsd

2.3.2 Dow Butadiene-Based Octene-1 Process

Dow has developed a process to make octene-1 only based on the telomerization of butadiene with methanol in the presence of a palladium catalyst. The chemistry of the complete reaction sequence is shown below:



$$2CH_2{=}CH{-}CH{=}CH_2 + CH_3OH \longrightarrow CH_3O{-}CH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2$$

$$H_3CO{-}CH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2 + 2H_2 \longrightarrow CH_3O{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

$$CH_3O{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow H_2C{=}CH{-}(CH_2)_5{-}CH_3 + CH_3OH$$

Q108_00101.0007.4105-3.cdx

Dow was scheduled to start-up a 50,000 metric ton per year octene-1 plant in Terragana, Spain using this butadiene based approach in 2007.

2.3.3 Sasol Heptene-1 to Octene-1 Process

As previously described, Sasol has been very successful in the octene-1 comonomer business. However, the capacity of Trains I and II combined is 96 thousand metric tons per year and this is bumping up against the limit of the octene-1 contained in Sasol's Secunda synfuels stream. One approach to overcome this limitation is to exploit the availability of unused heptene-1 in the Secunda synfuels stream. In order to transform heptene-1 to octene-1, five process steps are required:

- Separation of crude heptene-1
- Hydroformylation of heptene-1 to *n*-octanal
- Hydrogenation of *n*-octanal to 1-octanol
- Dehydration of 1-octanol to octene-1
- Final purification of octene-1 to comonomer grade

Sasol has announced that a new octene-1 plant using all of these process steps is under construction at Sasol's Secunda complex. This plant will be the third and largest of three octene-1 trains at that location, but the first to employ a hydroformylation step. Davy Process Technology is supplying the hydroformylation technology. The latest train will produce 100 thousand metric tons of octene-1 and was scheduled to go into operation during the second half of 2007, but is now expected to start-up in 2008.

3 ECONOMICS

Cost of production economics for the following LAO process technologies are included in this report:

3.1 Commercial Full Range

- Chevron Phillips Process
- INEOS Process
- Shell SHOP Process
- Idemitsu

3.2 Commercial Single Fraction or On-Purpose

- Chevron Phillips Hexene-1 via Ethylene Trimerization
- Sasol FT-Derived Hexene-1
- Sasol FT-Derived Octene-1
- Butene-1 via Extractive Distillation from Mixed C_4's
- Axens Butene-1 via Alphabutol process

3.3 Emerging On-Purpose Routes

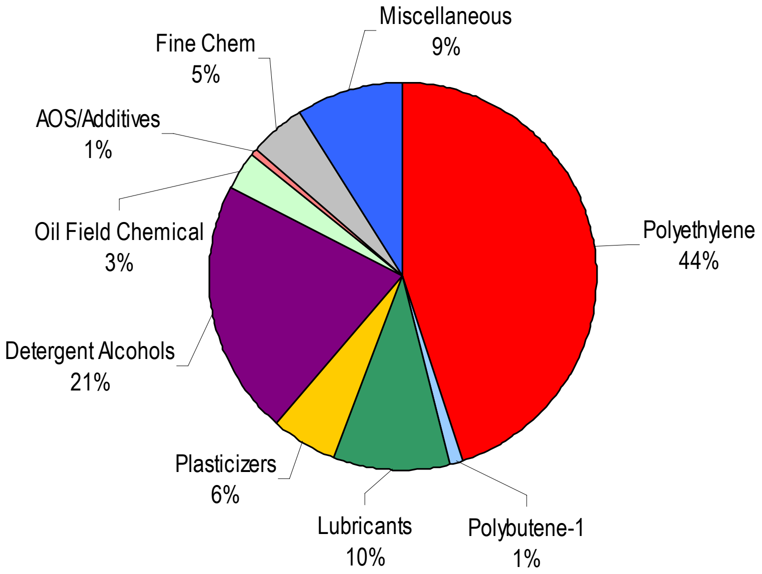
- Lummus Hexene-1 via Butene-1 Metathesis (CPT)
- Dow Octene-1 via Butadiene Telomerization
- Sasol Ocetene-1 via Heptene-1 Hydroformylation
- Sasol Octene-1 via Ethylene Tetramerization

4 COMMERCIAL ANALYSIS

The global demand for linear alpha olefins is about four million tons in 4.2 million tons. Butene-1, which is sourced from both on-purpose production and full range LAO plants, accounts for around 25 percent of demand. Demand is focused on LLDPE which dominates, accounting for about 35 percent of total demand consuming butene-1, octene-1 and hexene-1. Detergents are the second major end-use for LAOs, accounting for about 21 percent. This is followed by HDPE and synthetic lubricants.

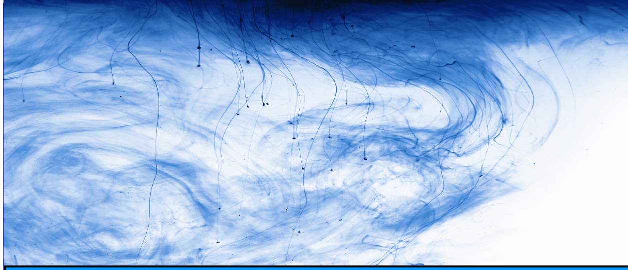
North America accounts for circa 48 percent of global LAO demand. However, over the forecast period to 2020, Asia is anticipated to grow strong growth well above the global average. By 2020, the region could account for around seventeen percent of the global total. In contrast, overall demand growth in developed economies will be in line with, or even below average GDP across all LAO fractions.

Figure 7 Linear Alpha Olefin Demand by End-Use
(2006 Estimate)



Q108_00101.0007.4105-Charts.xls\Fig 8.6

In general, developed economies are mature alpha olefins markets. In countries like China and India to a lesser extent, there is not only strong demand growth for petrochemicals in general, there is also an increased need for more sophisticated products and this impacts products across the whole LAO spectrum from plastics to detergents to lubricants, etc.



Nexant, Inc.

San Francisco
London
Tokyo
Bangkok
New York
Washington
Houston
Phoenix
Madison
Boulder
Dusseldorf
Beijing
Shanghai
Paris

www.chemsystems.com